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STRUCTURE OF TRANSITION STATES IN FORBIDDEN PERICYCLIC REACTIONS. THE SECOND-ORDER SIMILARITY APPROACH

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The recently proposed similarity approach to the Evans/Dewar concept of aromaticity of transition states was generalized by introducing the second-order similarity index. This generalization is especially convenient for the characterization of antiaromatic transition states in forbidden reactions since, owing to the partial incusion of electron correlation in the second-order index, the detailed specification of their structure in terms of the electron states of these biradicaloid species becomes possible. The results obtained are in complete agreement with the conclusions of independent quantum chemical analyses.

INTRODUCTION

One of the first attempts at a topological explanation of Woodward–Hoffmann rules is represented by Dewar's concept of aromaticity of transition states.[1] Based on the old intuitive idea by Evans and Warhurst,[2] this concept attempts to relate the ease of certain pericyclic reactions to the arrangement of corresponding transition states. Thus, e.g., the ease of most Diels–Alder reactions is, from this point of view, derived from the concept that the six-membered cyclic species formed on approaching the diene and dienophilic components is isoconjugated, i.e. topologically equivalent with aromatic benzene, and as a such should consequently be stabilized energetically. This intuitive parallel was revived by Dewar, who generalized it into the form of simple rule that all the allowed reactions proceed via aromatic transition states.

This simple idea was later supported theoretically by Aihara[3] and Van der Hart *et al.*[4] and recently also in our previous study,[5] in which a numerical quantitative evaluation of the expected similarity of transition states to aromatic and antiaromatic reference structures (for allowed and forbidden reactions, respectively) was achieved using the so-called similarity index.[6] Our aim in this study was to extend this previous work and to clarify some of its conclusions, expecially concerning the nature of transition states in forbidden reactions in terms of second-order similarity indices.[7] The main advantage of this new generalized description is that the partial inclusion of electron correlation in the second-order indices makes it possible to discriminate between the individual electron states of biradicaloid antiaromatic species corresponding to expected transition states of forbidden reactions, thus allowing a more detailed insight into the structure of these transition states.

THEORETICAL

Because of the close methodological parallel with our previous study[5] dealing with the characterization of transition-state structure in terms of first-order similarity index, we consider it convenient to recapitulate briefly the basic ideas of the similarity approach to the extent necessary for the purpose of this study. The basis of the proposed approach consists in the incorporation of the similarity indices[6] into the framework of the so-called overlap determinant method,[8] which is a general technique of describing the chemical reaction as a continuous transformation $R \rightarrow P$ of a reactant R into a product P. Using this approach, mathematically realized by the simple parametric equation

$$\Phi(\varphi) = \frac{1}{N(\varphi)}\left(\cos\varphi\Phi_R + \sin\varphi\Phi_P\right) \quad (1)$$

we discovered, in several previous studies[5,7,8] the important role of the critical structure $X(\pi/4)$, the properties of which are in many respects analogous to those of the critical structures on the potential energy hypersurface.[5] On the basis of this analogy, Dewar's concept of aromaticity of transition states was quantitatively examined by evaluating the 'similarity' between the

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critical structure $X(\pi/4)$ [characterized by the density matrix $\Omega(\pi/4)$], representing the topological model of the transition states, and the appropriate aromatic and/or antiaromatic reference structures. This similarity is quantitatively expressed by the term

$$r_{\neq,\mathrm{ref}} = \frac{1}{N_{\neq,\mathrm{ref}}}\,\mathrm{Tr}\,\Omega(\pi/4)\,\Omega_{\mathrm{ref}} \qquad (2)$$

the actual values of which do indeed confirm the expected similarity of transition states to aromatic standards in allowed reactions, whereas in forbidden reactions the similarity to antiaromatic reference structures dominates.

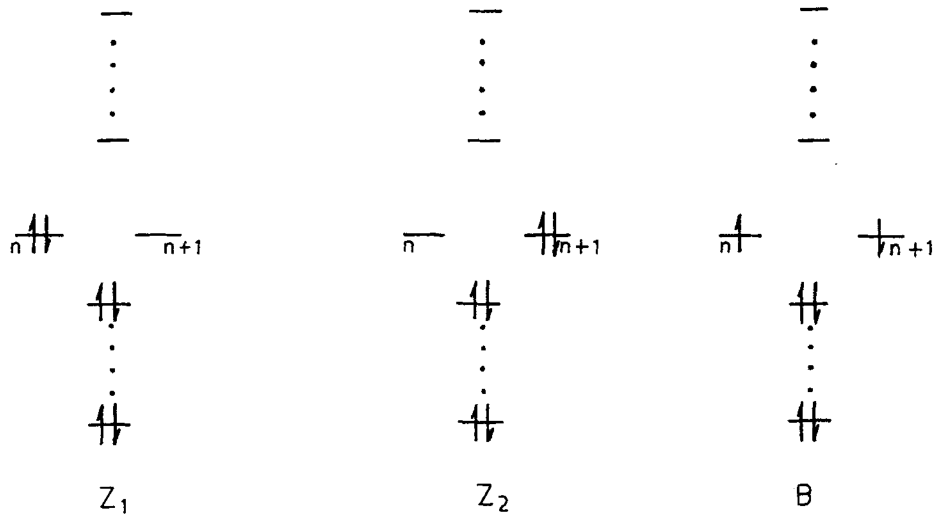
Our aim here is to pursue the general philosophy of the above similarity approach and to complement the general findings of the previous study by some new, and in our opinion interesting, conclusions expecially concerning the structure of antiaromatic transition states in forbidden reactions. It appears that the original conclusions concerning the dominant similarity of transition states to antiaromatic reference structures can be complemented by new information arising from the proper generalization of the similarity approach.

The basic idea of this generalization arises from the following simple considerations. Antiaromatic structures playing the role of transition states in forbidden reactions are species with considerable biradicaloid character and as such cannot be satisfactorily described by the usual one-electron approximation. As demonstrated by Salem and Rowland[9] and more recently also by Bonačič-Koutecký *et al.*,[10] the correct treatment of these species requires the existence of several electron states compatible with various possibilities of distributing two unpaired electrons into two degenerated molecular orbitals to be taken into account (Scheme 1). There are generally three such states; two of them correspond to structures of zwitterionic type and the third is a covalent biradical. According to notation introduced by Bonačič-Koutecký *et al.*,[10] these states are denoted $(Z_1 + Z_2)$, $(Z_1 - Z_2)$ and B, where the meaning of this notation becomes clear from the corresponding wavefunctions and Scheme 1.

$$\begin{aligned}\Phi_{(Z_1 \pm Z_2)} &= \frac{1}{\sqrt{2}}\Big(|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\cdots\varphi_n\bar{\varphi}_n| \\ &\qquad \pm |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\cdots\varphi_{n+1}\bar{\varphi}_{n+1}|\Big) \\ \Phi_{\mathrm{B}} &= \frac{1}{\sqrt{2}}\Big(|\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\cdots\varphi_n\bar{\varphi}_{n+1}| \\ &\qquad \pm |\varphi_1\bar{\varphi}_1\varphi_2\bar{\varphi}_2\cdots\varphi_{n+1}\bar{\varphi}_n|\Big)\end{aligned} \qquad (3)$$

Since, however, all these states are indistinguishable at the level of first-order density matrix, it is apparent that on using the similarity index in equation (2), the important part of the structural information is inherently lost. In order to remedy this inherent loss of information, we propose here a straightforward generalization, consisting in the use of a second-order similarity index,[7,11] defined in terms of pair density matrices instead of first-order density matrices:

$$g_{\mathrm{AB}} = \frac{\int \bar{\rho}_{\mathrm{A}}(1,2)\bar{\rho}_{\mathrm{B}}(1,2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2}{\left[\int \bar{\rho}^2_{\mathrm{A}}(1,2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\right]^{1/2}\left[\int \bar{\rho}^2_{\mathrm{B}}(1,2)\,\mathrm{d}\tau_1\,\mathrm{d}\tau_2\right]^{1/2}} \qquad (4)$$



Scheme 1

As a consequence, this index is able to describe the subtler differences in the electron structure arising, as in the case of electronic states of biradicaloid species, from the partial inclusion of electron correlation. In our case the original general expression (4) for the similarity index g_{AB} has to be rewritten in the form

$$g_{\neq,\mathrm{ref}} = \frac{\int \tilde{\rho}_{\pi/4}(1,2)\tilde{\rho}_{\mathrm{ref}}(1,2)\,d\tau_1\,d\tau_2}{\left[\int \tilde{\rho}^2_{\pi/4}(1,2)\,d\tau_1\,d\tau_2\right]^{1/2}\left[\int \tilde{\rho}^2_{\mathrm{ref}}(1,2)\,d\tau_1\,d\tau_2\right]^{1/2}} \tag{5}$$

where $\tilde{\rho}_{\pi/4}(1,2)$ denotes the spinless pair density matrix of the critical species $X(\pi/4)$ defined in terms of generalized wavefunction (1) for $\varphi = \pi/4$:

$$\tilde{\rho}_{\pi/4}(1,2) = \frac{N(N-1)}{2}\int \Phi^2(\pi/4)\,d\sigma_1\,d\sigma_2\,dx_3\,dx_4\cdots dx_N \tag{6}$$

and $\tilde{\rho}_{\mathrm{ref}}$ is the analogously defined pair density matrix of the corresponding reference structure. As already stressed above, in the case of forbidden reactions these reference structures are typical biradicaloid species (cyclobutadiene and Möbius benzene for four- and six-electron transformations, respectively), the specific feature of which is the presence of several low-lying electronic states[9,10] differing in the distribution of two unpaired electrons between two degenerate molecular orbitals (Scheme 1). Since owing to partial inclusion of electron correlation the pair density matrix correctly reflects the differences in the electron structures of these species, it is possible to expect that the comparison of corresponding pair densities for individual electron states of the reference structure with the pair density of the transition state via the similarity index in equation (5) will make it possible to specify the electron state of the reference species which approximates the structure of the transition state the most closely.

Table 1. Calculated values of second-order similarity index, $g_{\neq,\mathrm{ref}}$, between the antiaromatic reference standard and the critical structure $X(\pi/4)$ modelling the transition state in a series of selected forbidden pericyclic reactions

Reaction	Mechanism	$g_{\neq,\mathrm{antiarom}}$		
		B	$Z_1 - Z_2$	$Z_1 + Z_2$
Ethene + ethene → cyclobutane	s + s	0·920	0·920	1·000
Butadiene → cyclobutene	Disrotation	0·879	0·879	0·947
Diels–Alder reaction	s + a	0·932	0·938	0·954
Hexatriene → cyclohexadiene	Conrotation	0·916	0·916	0·933
Cope rearrangement	s + a	0·933	0·944	0·959
Butadiene → bicyclobutane	s + s	0·442	0·471[a]	0·467

[a] The dominant similarity in this case is different from the general trend observed in all remaining reactions, but the analogous situation suggesting a certain delicateness of this reaction was already observed in the case of allowed reactions.[5]

The final expressions for the corresponding similarity indices $g_{\mathrm{ref},\neq}$ for all the individual electron states of the reference standard are given in the Appendix. The values of this index calculated on the basis of these expressions for several forbidden pericyclic reactions are collected in Table 1. In order to maintain continuity with our previous study[5] dealing with first-order similarity analysis, the same series of reactions was chosen. This allows us also to reduce the necessary technical details of the calculations, which can be found elsewhere.[6] Here we only recall that the wavefunctions of corresponding molecular species were calculated by a simple HMO method compatible with the topological nature of the approach.

RESULTS AND DISCUSSION

Let us discuss now some general conclusions arising from Table 1. The most interesting in this connection is the comparison of indices $g_{\neq,\mathrm{ref}}$ characterizing the similarity of expected transition states to individual electron states of antiaromatic reference standards. As can be seen, the situation in all reactions is completely analogous and the transition states are always found to be best approximated by the zwitterionic state $Z_1 + Z_2$ of the reference standard. This result is, however, very surprising since, e.g., in four-electron transformations the zwitterionnic $Z_1 + Z_2$ state does not describe the ground state of cyclobutadiene (which is a natural antiaromatic reference standard) but rather the highest excited singlet state S_2. In analysing this surprising result we have assumed that its origin apparently lies in the fact that the critical structure $X(\pi/4)$, originally expected to approximate the transition state, does not in this case describe the ground state of the transition state but some of its excited states. In order to explain this circumstance, it is necessary to analyse first the form of equation (1), from which our conclusions were derived.

In connection with equation (1) it is possible to see that the desired aim, the transformation of the reactant into the product, can be achieved not only by the variation of φ within the interval $(0, \pi/2)$, but since the function $-\Phi_P$ is physically indistinguishable from the function Φ_P, the same result can also be obtained if the reaction coordinate φ varies within the interval $(0, -\pi/2)$. The existence of these two alternative reaction paths was mentioned in a previous paper,[12] where the problem of non-uniqueness of the transformation equation (1) was discussed in detail. In this discussion we have demonstrated that the 'correct' direction of the reaction path can be deduced from the requirement for minimal changes of electron configurations (the so-called least-motion principle[13] and that this direction depends on the value of the overlap integral S_{RP}. If $S_{RP} > 0$, which is the case with all allowed reactions, the preferred reaction path is the one with φ varying in the interval $(0, \pi/2)$, whereas for the alternative path corresponding to the variation of φ within the interval $(0, -\pi/2)$, the electron reorganization attains its maximum. In harmony with this finding, the aromatic transition states in allowed reactions were successfully modelled by the critical structure $X(\pi/4)$.[5]

A more interesting situation is in the case of forbidden reactions, where owing to the zero value of the overlap S_{RP}, the two alternative reaction paths degenerate and become indistinguishable. This seems to suggest that the critical structures $X(\pi/4)$ and $X(-\pi/4)$ should be equivalent, so that the transition state could be modelled equally well by either of them. The situation is slightly more complex, however. The expected equivalence of critical structures $X(\pi/4)$ and $X(-\pi/4)$, confirmed in a number of previous studies,[5,12,14,15] is not, apparently, entirely complete and in our approach here the differences between the two reaction paths start to appear. These differences can be best demonstrated by comparison of actual values of the similarity indices $g_{\neq,\mathrm{ref}}$ corresponding to the critical structure $X(-\pi/4)$ (Table 2) with those in Table 1. The most important difference concerns the systematic shift of the dominant similarity from the original zwitterionic $Z_1 + Z_2$ state to the state $Z_1 - Z_2$. This result is very interesting since it demonstrates that in contrast to previous studies,[5,14,15] the conclusions of the present analysis do depend on which of the critical structures, $X(\pi/4)$ or $X(-\pi/4)$, is used as a model of the transition state.

Table 2. Calculated values of second-order similarity index, $g_{\neq,\mathrm{ref}}$, between the antiaromatic reference standard and the critical structure $X(-\pi/4)$ representing an alternative model of the transition state in a series of forbidden pericyclic reactions

Reaction	Mechanism	$g_{\neq,\mathrm{antiarom}}$		
		B	$Z_1 - Z_2$	$Z_1 + Z_2$
Ethene + ethene → cyclobutane	s + s	0·840	1·000	0·920
Butadiene → cyclobutene	Disrotation	0·811	0·955	0·849
Diels–Alder reaction	s + a	0·915	0·956	0·938
Hexatriene → cyclohexadiene	Conrotation	0·901	0·938	0·917
Cope rearrangement	s + a	0·918	0·959	0·944
Butadiene → bicyclobutane	s + s	0·506	0·540	0·535

As a consequence of this ambiguity, the question thus arises of which of the two alternative assignments is to be regarded as the correct one. Similarly to the case of allowed reactions, such a decision does not arise from the approach itself, and some external additional information is generally required. This usually represents no problem since the desired information can be obtained, as in the case of allowed reactions, from simple qualitative considerations (least motion principle[13]), or from direct quantum chemical calculations. This is also the case here, where the desired information is provided by a quantum chemical study[16] of the thermally forbidden cyclization of butadiene to cyclobutene. From this study it follows that the ground state of the transition state should correspond to the ground state of cyclobutadiene, which is the $Z_1 - Z_2$ state. We can therefore expect that the correct reaction path is that for which the antiaromatic transition state will be best approximated just by the $Z_1 - Z_2$ state of the biradicaloid reference structure. Since, however, just such a kind of correspondence is observed in Table 2, it is possible to expect that the transition states in forbidden reactions should be better approximated by the structure $X(-\pi/4)$ characterised by the wavefunction (7a) than by the original structure $X(\pi/4)$ [equation (7b)], which rather describes the excited state of the transition state.

$$X(-\pi/4) = \frac{1}{\sqrt{2}}\left(\Phi_R - \Phi_P\right) \tag{7a}$$

$$X(\pi/4) = \frac{1}{\sqrt{2}}\left(\Phi_R + \Phi_P\right) \tag{7b}$$

This result is very interesting since the same conclusions concerning the form of the wavefunctions of the transition state[*] have already been found in a much more sophisticated TC-SCF study by Bofill *et al.*[17] In this connection, however, it is important to note that whereas these direct calculations were restricted only to relatively small model systems, the simplicity of our model made it possible to analyse also systems which lie far beyond the scope of current quantum chemical calculations. In addition to this remarkable simplicity, allowing the approach to be used with extensive series of reactions, the formalism presented brings yet another important advantage, namely that the possibility of analysing a broader series of reactions allows us to discover general trends and tendencies which

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[*] The structures corresponding to these 'transition states' are not in fact true saddle points but higher order critical points. The possible semantic complications arising from the fact that Dewar's classification operates with the term transition state for all types of critical points irrespective of whether they are true saddle points are discussed in detail in Ref. 5.

would otherwise be difficult to elucidate. Thus, for example, in our case the parallel between the transition state and the $Z_1 - Z_2$ state of the antiaromatic reference standard was directly proved by quantum chamical calculations on only a few particular systems,[16,17] and only the analogous behaviour discovered by our approach within the whole series allowed us to give this particular observation a more general unifying character. The importance of such generalizations can be also demonstrated with our recent study,[11] in which the analogous similarity approach allowed us to discover the interesting systematic regularities in the manifestations of the effects of electron correlation in various types of pericyclic reactions. In connection with these interesting conclusions it is necessary, however, to be aware that the aim of the similarity approach is not to replace direct quantum chamical calculations, but rather to complement their results by simple and easily accessible generalizations, which for chemistry are often more valuable than the 'precise', but isolated, results on individual particular systems.

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APPENDIX

The practical calculation of the similarity index g is based on the formal transcription of the original definition relation (5) in terms of expansion of the pair densities in the basis of atomic orbitals:

$$\tilde{\rho}(1,2) = \sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta} \tilde{\Omega}_{\alpha\beta\gamma\delta}\chi_{\alpha}(1)\chi_{\beta}(1)\chi_{\gamma}(2)\chi_{\delta}(2) \quad (A.1)$$

Using this expansion and taking into account the symmetry of the matrix $\tilde{\Omega}$ with respect to the permutation $\alpha \leftrightarrow \beta$ and $\gamma \leftrightarrow \delta$, the original definition equation (5) can be rewritten in the form

$$g_{\neq,\mathrm{ref}} = \frac{\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}\left[\tilde{\Omega}(\pi/4)\right]_{\alpha\beta\gamma\delta}\left[\tilde{\Omega}_{\mathrm{ref}}\right]_{\alpha\beta\gamma\delta}}{\left(\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}\left[\tilde{\Omega}(\pi/4)\right]^2_{\alpha\beta\gamma\delta}\right)^{1/2}\left(\sum_{\alpha}\sum_{\beta}\sum_{\gamma}\sum_{\delta}\left[\tilde{\Omega}_{\mathrm{ref}}\right]^2_{\alpha\beta\gamma\delta}\right)^{1/2}} \quad (A.2)$$

Since the form of the pair density $\tilde{\Omega}(\pi/4)$ has already been presented in a previous study,[14] it is only necessary to specify the form of the pair densities $\tilde{\Omega}$ for the antiaromatic reference standards. The structure of these species was discussed by Salem and Rowland[9] and Bonačič-Koutecký *et al.*,[10] who demonstrated that the proper description of these biradicaloid species requires the existence of several electron states compatible with the different possibilities of distributing the two unpaired electrons into two degenerate molecular orbitals to be taken into account (Scheme 1). On the basis of this analysis, the individual states constructed from the basis configurations Z_1, Z_2 and B are denoted $(Z_1 - Z_2)$, $(Z_1 + Z_2)$ and B.

Taking into account that the basis electron configurations Z_1, Z_2 and B contributing to the formation of individual electron states differ in the occupation numbers of the degenerate pair of molecular orbitals $N/2$ and $N/2+1$ ($[2,0] \sim Z_1$, $[0,2] \sim Z_2$, $[1,1] \sim B$), the final expressions for the matrix elements of the pair density $\tilde{\Omega}_Q(Q = Z_1 \pm Z_2, B)$ are given in the equations

$$\begin{aligned}[\tilde{\Omega}_{Z_1 \mp Z_2}]_{\alpha\beta\gamma\delta} = \tfrac{1}{2}\{ & [\Omega'_{Z_1}]_{\alpha\beta\gamma\delta} + [\Omega'_{Z_2}]_{\alpha\beta\gamma\delta} \\ & \mp (d_{\alpha N/2}d_{\beta N/2+1} + d_{\alpha N/2+1}d_{\beta N/2})(d_{\gamma N/2}d_{\delta N/2+1} \\ & + d_{\gamma N/2+1}d_{\delta N/2})\}\end{aligned} \quad (A.3)$$

$$\begin{aligned}[\tilde{\Omega}_{B}]_{\alpha\beta\gamma\delta} = {} & [\Omega'_{B}]_{\alpha\beta\gamma\delta} - \tfrac{1}{2}(d_{\alpha N/2}d_{\beta N/2}d_{\gamma N/2}d_{\delta N/2} \\ & + d_{\alpha N/2+1}d_{\beta N/2+1}d_{\gamma N/2+1}d_{\delta N/2+1}) \\ & + \tfrac{3}{4}(d_{\alpha N/2}d_{\delta N/2+1} + d_{\alpha N/2+1}d_{\delta N/2}) \\ & \times (d_{\gamma N/2}d_{\beta N/2+1} + d_{\gamma N/2+1}d_{\beta N/2})\end{aligned} \quad (A.4)$$

where d are LCAO expansion coefficients of corresponding molecular orbitals and the matrix $\Omega'_Q(Q = Z_1 \pm Z_2, B)$ is given in terms of first-order density matrices Ω_Q by the equation

$$\begin{aligned}[\tilde{\Omega}_Q]_{\alpha\beta\gamma\delta} = {} & (\Omega_Q)_{\alpha\beta}(\Omega_Q)_{\gamma\delta} \\ & - \tfrac{1}{4}[(\Omega_Q)_{\alpha\gamma}(\Omega_Q)_{\beta\delta} + (\Omega_Q)_{\beta\gamma}(\Omega_Q)_{\alpha\delta}]\end{aligned} \quad (A.5)$$